

EXPERIMENTAL STUDIES OF EQUILIBRIA IN C-H-O PLASMAS\*

by

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ABSTRACT

Six organic oxygen compounds, representing six points on a C-H-O ternary diagram, were subjected to a high energy electrodeless R.F. discharge. The concentrations of the gaseous products were compared to the concentrations computed for thermodynamic equilibrium at the experimental conditions. The results show the major products to be present in approximately the same proportions as calculated, and the predicted asphalt threshold is also shown to exist. The nature of the solid product formed is discussed in terms of present theories on the origin of hydrocarbons in carbonaceous chondrites. A quasi-equilibrium is suggested to account for the formation of products rather than a true thermodynamic equilibrium.

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## INTRODUCTION

Since Oparin 1938 first proposed that the prebiological atmosphere of the Earth was of a reducing nature, many workers Miller (1955), Ponnampertuma, et al. (1963) and Sanchez, et al. (1966), have shown that complex organic compounds can be synthesized in these conditions if sufficient energy is supplied to the system. The success of these experiments has suggested that the concentrations of complex mixtures of gases can be calculated for a thermodynamic equilibrium, and the predicted amounts of the molecules formed may be compared to the experimental results.

The computational method followed in the present work is that developed by White, et al. (1958), in which the equilibrium concentrations of many compounds are calculated by minimizing the total free energy of the system. The distribution of these compounds at equilibrium is independent of the specific reactions occurring, the only requirement being the existence of at least one reversible reaction path from the major constituent by which each compound can be formed. This reaction path is dependent only on pressure, temperature and elemental composition, and therefore the equilibrium constants of all possible reactions are satisfied.

Dayhoff, et al. (1964) and Eck, et al. (1966) have developed such a computer program by which the equilibrium concentrations of over 500 compounds containing up to 25 elements can be computed for a wide range of temperatures and pressures. The present work involved selecting a number of organic compounds and then computing the equilibrium concentrations of these compounds for the six C-H-O

elemental compositions which correspond to the compounds used.

The energy required to overcome the activation energies for the various reactions was supplied by an electrodeless R.F. discharge. When a tube of gas is inserted into a wire helix which is excited with R.F., it acts as a secondary in a transformer, and the gas is partially ionized as a result of dielectric loss. If the excitation is great enough the ionization is essentially complete and the resultant plasma approximates to a shorted turn in the inducing coil.

Dayhoff, et al.(1964) showed that C-H-O systems, either alone or containing other elements, could be represented on ternary diagrams, each diagram having thresholds where the concentrations of compounds change by several orders of magnitude, see Fig. I. The oxygen threshold is represented by the  $\text{CO}_2\text{-H}_2\text{O}$  line, and below this threshold only  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{O}_2$  can exist in appreciable concentration. The position of the asphalt threshold changes with temperature and pressure; for elemental compositions above this line, benzene and a large number of polynuclear aromatics can form. For simplicity, these polynuclear aromatics are grouped under the name asphalt, which is a composite compound represented by a formula  $\text{C}_{22}\text{H}_{12}$ , having 100 isomers. The free energy was calculated using the group contribution method of Van Krevelin, et al. (1951).

Graphite may be considered to be the end product of the polymerization of asphalt, and even at fairly high temperatures, the

activation energy for its formation seems to be very high, and for this reason it is omitted from the computations.

#### EXPERIMENTAL PROCEDURE

The apparatus used is shown in Fig. II. The R.F. generator was operated at a frequency of 10 MHz with a maximum D.C. input power of 1125 watts. The system was approximately 60% efficient in converting the D.C. to R.F. and coupling the R.F. to the plasma. Power transfer from the R.F. generator to the plasma depends on proper impedance matching, and, since the frequency of the generator could not be altered, correct matching could only be made by adjusting the pressure of the gas, the optimum pressure being in the region of 20 torr.

Pure compounds were used for the gas samples so that the elemental composition was accurately known, and a flow system was employed so that the formation of a solid deposit did not change the overall composition of the reacting gas by a very large degree.

Two types of plasma were observed. The first had the appearance of a glow discharge with a low intensity blue glow. The second type of plasma was termed a 'flame plasma' since a dense pink flame was formed in the center of the reaction tube. Samples producing a glow discharge did not form a solid product while those producing a flame plasma deposited a solid almost immediately on the walls of the reaction tube; the flame was therefore probably

caused by incandescent particles formed from reactions in the plasma. A glow discharge was produced by each sample at low pressure, but in the region between 12 and 17 torr. some samples gradually transformed from a glow discharge to a flame plasma, while others remained unchanged. Above 20 torr., a pressure was reached with each sample where the plasma would self-destruct. It was also noted that a sufficiently high vapour flow rate was necessary for the production of a flame plasma, and liquids with low vapour pressures could not be used for these experiments.

Eight compounds were studied, representing seven C-H-O compositions as denoted by the letters A through G on the ternary diagram on Fig. I; these compounds and their elemental compositions are given in Table I. Composition G represents the two isomers methyl acetate and ethyl formate whose gas products were quantitatively compared.

At the end of the experiment, part of the gas sample was collected in a 1-meter I.R. gas cell; the apparatus was then filled with 300 torr. of helium, and a sample of the resultant gas was collected in a gas pipette for analysis by gas chromatography. A Varian Aerograph 1520B gas chromatograph was used, with a Linde 5B molecular sieve column and a thermal conductivity detector.

## RESULTS

The I.R. spectra and gas chromatograms for compositions B through G appeared to be essentially the same with large amounts of  $H_2$ ,  $CH_4$ ,  $CO$  and  $C_2H_2$  and relatively smaller quantities of  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_8$  and  $CO_2$ . The quantities of acetylene, ethylene and ethane were observed in the order  $C_2H_2 > C_2H_4 > C_2H_6$ .

The GC detected only  $\text{CO}_2$ , CO and  $\text{H}_2$  at composition A, and the presence of water was detected by mass spectrometry in a gas sample which was not passed through the  $\text{CO}_2$ -acetone trap.

The products from the two isomers of composition G were compared by determining a percentage of the total area under each peak in the GC. The results in Table II show that the composition of the gas mixtures are largely independent of the nature of the starting material but depend on its elemental composition.

#### NATURE OF THE SOLID DEPOSIT

The difference between the nature of the plasmas seen with compositions A, B and C and with D, E and F demonstrate the existence of the asphalt threshold predicted by Dayhoff, et al.(1964). Graphite could not be detected in large quantity in the solid deposit, which lends credence to the approximation made by Dayhoff as to its rate of formation. The actual nature of the solid deposit, however, was difficult to determine, and different colored regions could be observed on the walls of the tube. Black rings formed at the top and bottom of the tube, and between these the color would vary from brown to light yellow. Most parts of the deposit would fluoresce green in U.V. light indicating the presence of aromatics. The yellow solid was mainly an aliphatic polymer, while the other areas contained asphaltic compounds and a very small amount of finely divided graphite. It was found that the solid was partially soluble in benzene, the solution being highly fluorescent; the I.R. spectrum of a mull of this fraction in

1,3: hexachlorobutadiene in the region from  $3300-2900\text{ cm}^{-1}$  showed the presence of more aromatic than aliphatic C-H bonds. Analysis of this fraction by thin-layer and gas chromatography was rather inconclusive, but such polynuclear aromatics as pyrene, chrysene, coronene and fluoranthene have been identified. The fraction which is insoluble in benzene fluoresces a very light blue with U.V. light and the I.R. spectrum indicates predominantly paraffinic C-H bonds. This is a similar result to that found by many workers investigating the polymerization of acetylene to cuprene by, for example silent and semi-corona discharge, Glockler, et al. (1943), electron irradiation, Jones (1960), and x-ray polymerization, Lind, et al. (1926).

It is interesting to compare the solid product obtained in these experiments with the extracted from carbonaceous chondrites. Anders 1963 states that most of the hydrocarbons he finds are saturated, and there is little evidence for polynuclear aromatics with more than two rings. Briggs 1962 also states that there is evidence of completely insoluble organic material in carbonaceous chondrites, which appears to be a high molecular weight hydrocarbon polymer similar to the benzene insoluble fraction formed in the present experiments. However in a later paper, Briggs (1962) report that aromatics are present and form a fairly high proportion of the total hydrocarbon content, along with the saturated and unsaturated aliphatic polymers; 95% of the organic matter he finds is unidentified. Hayes (1967), in a review article, summarizes the recent investigations into the organic constituents of meteorites, and comes to the

conclusion that the results of the many analyses of carbonaceous chondrites show about 30% of the total carbon present to be extractable into organic solvents, and consists of both aliphatic and aromatic hydrocarbons; the remaining 70% appears to be tied up in an organic polymer.

Most recently, Studier, et al. (1968) made a detailed study of the composition of hydrocarbons found in carbonaceous chondrites and of hydrocarbons made synthetically from mixtures of carbon monoxide and deuterium using iron meteorite powder as catalyst. At low temperatures, straight chain paraffins and olefins preconvert synthetically, with a slow conversion to aromatics on sustained reheating, while at 900°C polynuclear aromatics were obtained in high yield. They reconcile these results with the analysis of the organic constituents of carbonaceous chondrites by proposing a two-stage mechanism. The first step involves a Fischer-Tropsch synthesis which can occur at high H-C ratios; the hydrocarbons condense in the meteorite and become isolated from the hydrogen-rich gas phase. In the second stage, since the composition of the carbon-hydrogen system now lies in the asphalt region, equilibration can occur over a long time scale causing the conversion of aliphatic to aromatic molecules.

The results of the present investigation can be reconciled with the theories of Studier, et al. (1968) and the observations of the other workers. The black rings, which form on the walls of the



reaction tube and consist largely of polynuclear aromatics, may be considered to be formed by equilibrium processes, whereas the lighter-colored rings containing predominantly aliphatic hydrocarbons are formed close to the center of the plasma and condense before equilibrium is attained.

### COMPARISON WITH COMPUTATIONS

For compositions A through F, concentrations of over thirty compounds were computed for thermodynamic equilibrium at temperatures between 500° and 2000°K. All compounds were assumed to be in the gas phase with a total pressure of 20 torr. Five major compounds were selected for a comparison between computed and experimental concentrations; these are hydrogen, methane, acetylene, carbon monoxide and carbon dioxide. Their computed concentrations at temperatures from 500° to 2000°K are shown in Table III together with the observed concentrations calculated from the area under the peaks on the gas chromatogram.

It may be seen that the major species at 500°K are completely different from those over 1000°K. For compositions in the asphalt region, methane and CO<sub>2</sub> are the major compounds at 500°K, but hydrogen and CO became dominant above 1000°K, while above 1400°K CH<sub>4</sub> and CO<sub>2</sub> decrease to almost negligible amounts. At still higher temperatures, acetylene becomes an important constituent.

The results for compositions in the asphalt region, D, E and F, are best explained by a temperature in the range 1300°-1500°K

whereas the effective temperature for compositions B and C seems to be nearer  $1000^{\circ}\text{K}$ , although the high acetylene concentration for these compounds presents an anomaly. The effective temperature at composition A is indefinite since the mole fractions of the major compounds cannot be specified within a temperature range. The temperature of the glow discharge produced by A, B and C is expected to be lower than the temperature of the flame plasma produced by D, E and F since the glow discharge is neither as dense nor as well defined as the flame plasma.

It was not possible to measure the temperature of the plasma, since electrical methods must be eliminated because of the field produced by the R.F. coil and optical methods cannot be used because of the asphalt deposit. It is also not possible to say precisely where the reactions are occurring, and there must be a fairly steep temperature gradient from the center of the coil along the reaction tube. The fact that solid formation is seen to occur at the center of the coil shows that considerable reaction must occur in this region. However as the particles flow through this region they must still be in a highly excited state, and reaction can occur at positions further along the reaction tube.

Estimates of the temperature at the center of similar plasmas have been made by Dodonova (1954) and Mould, et al. (1960) who report that the translational temperature is in the range  $4000-2000^{\circ}\text{K}$ . This may be used to explain the large amount of acetylene measured in these experiments; it is postulated that the equilibrium is very

nearly complete in the central region of the plasma, and is modified with the temperature gradient as the gas flows along the tube, until there is no longer a sufficient number of molecules in an excited state to overcome the activation energy for the reaction.

Thus the product concentration cannot be adequately explained by a true thermodynamic equilibrium at a particular temperature, but is better explained in terms of a quasi-equilibrium along a temperature gradient.

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## LIST OF FIGURES

Figure I C-H-O Ternary Diagram at 0.026 atm pressure and 1200°K.

Figure II Apparatus used in the Discharge Experiments

1. R. F. Oscillator
2. Helical Colper Coil
3. Reaction Tube
4. Air Fan
5. 12-liter Reservoir
6. Bleed Valve
7. Stopcock
8. Diaphragm Pressure Gauge
9. Sample Container
10. Helium Cylinder
11. CO<sub>2</sub> - Acetone Trap
12. Gas Pipette
13. I. R. Gas Cell
14. Liquid Nitrogen Trap
15. Rotary Vacuum Pump

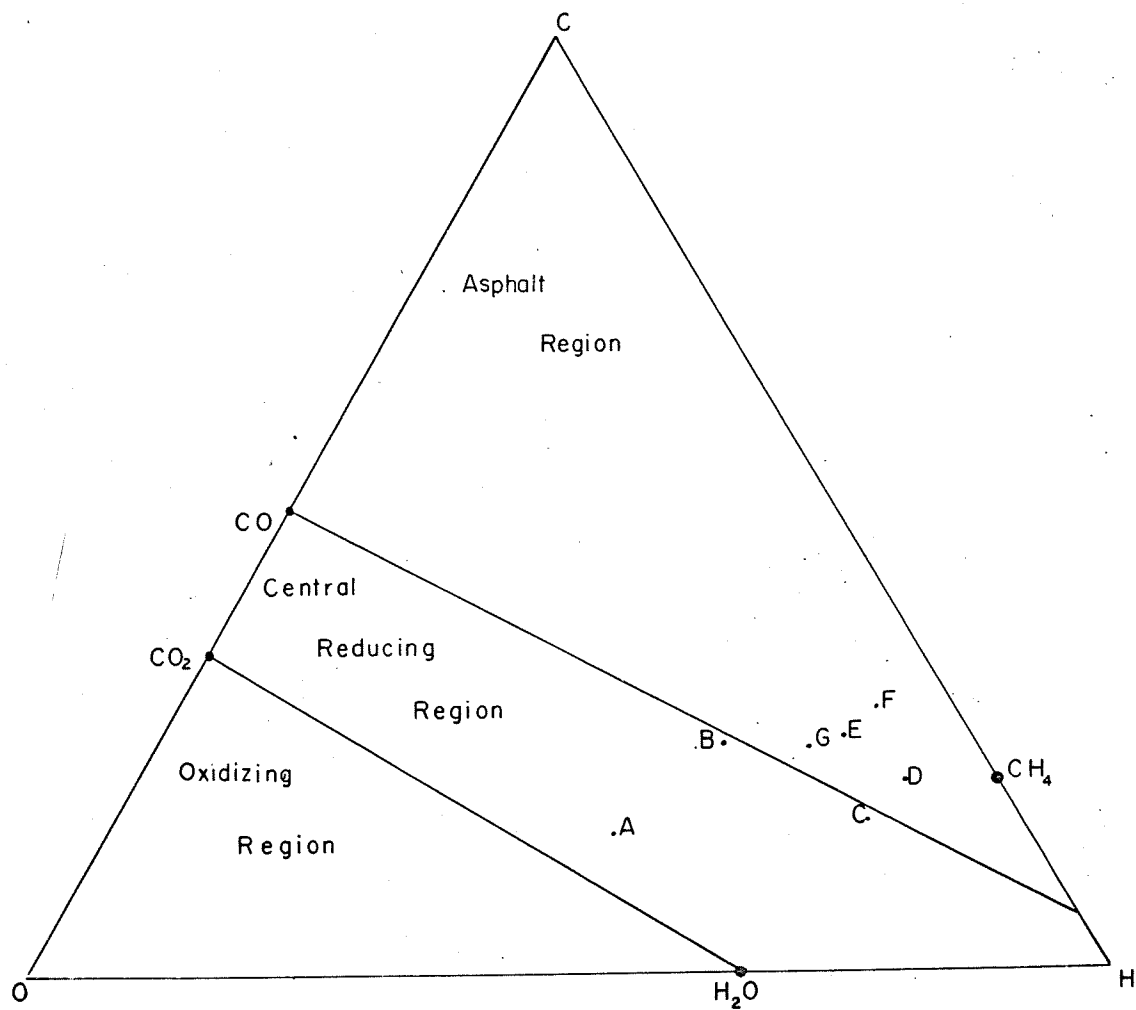


Figure 1

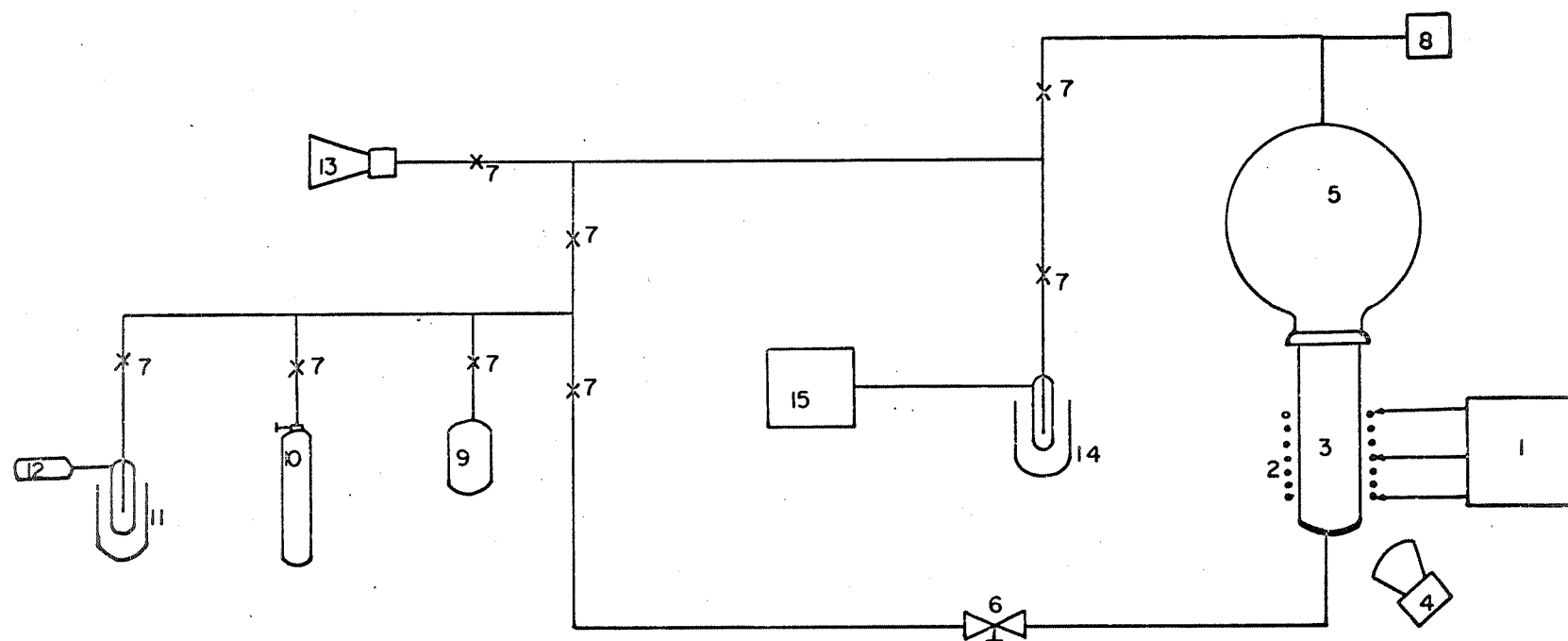


Figure 11



TABLE I

Experimental C-H-O Compositions Used in the Plasma Reactions

Composition	Compound	% Carbon	% Hydrogen	% Oxygen
A	Formic Acid	20	40	40
B	Acetic Acid	25	50	25
C	Methanol	16.7	66.7	16.7
D	Ethanol	22.2	66.7	11.1
E	Acetaldehyde	28.6	57.2	14.3
F	Acetone	30	60	10
G	Methyl Acetate	27.3	54.6	18.2
	Ethyl Formate			

TABLE II

Comparison of the Relative Distribution of Products from Two Isomers

<u>Peak Component</u>	<u>Ethyl Formate</u>	<u>Methyl Acetate</u>
H <sub>2</sub>	1.7%	2.0%
CH <sub>4</sub>	2.2	2.2
CO	77.2	75.3
C <sub>2</sub> H <sub>6</sub>	0.4	0.4
C <sub>3</sub> H <sub>8</sub> , CO <sub>2</sub>	1.2	0.7
C <sub>2</sub> H <sub>4</sub>	1.5	1.1
C <sub>2</sub> H <sub>2</sub>	15.8	18.2

TABLE III

The Production of Simple Molecules from C-H-O Systems

Composition	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	CO	CO <sub>2</sub>	Asphalt
A	***	-	-	-	-	***	***	-
B	***	*	*	*	*	***	*	-
C	***	*	*	*	**	***	*	-
D	***	*	*	*	**	***	-	*
E	***	*	*	*	**	***	-	*
F	***	*	*	*	**	***	-	*

\*\*\* Between 20 and 100%

\*\* Between 2 and 20%

\* Detectable, below 2%

- Not detected

TABLE IV

Comparison of Mole Fractions Between Experimental and  
Computed Data

Temperature °K	H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>
<u>Composition A</u>					
500	.0393	.0005	.7275	.2328	-
1000	.3506	.2987	.3506	-	-
1100	.3333	.3333	.3333	-	-
1200	.3151	.3699	.3151	-	-
1300	.3056	.3889	.3056	-	-
1400	.2857	.4286	.2857	-	-
1500	.2557	.4286	.2857	-	-
2000	.2537	.4925	.2537	-	-
Experimental	.354	.385	.263	n.o.	n.o.
<u>Composition B</u>					
500	.0026	.0059	.4907	.5008	-
1000	.4984	.4984	.0011	.0020	-
1100	.4996	.4996	.0002	.0005	-
1200	.4999	.6999	.0001	.0002	-
1300	.5000	.5000	-	.0001	-
1400	.5000	.5000	-	-	-
1500	.5000	.5000	-	-	-
2000	.5000	.500	-	-	-
Experimental	.485	.459	.014	.007	.035

TABLE IV (cont.)

Temperature °K	H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>
<u>Composition C</u>					
500	.0647	.0003	.2445	.6904	-
1000	.6647	.3323	.0008	.0021	-
1100	.6695	.3298	.0002	.0006	-
1200	.6698	.3299	-	.0002	-
1300	.6699	.3300	-	.0001	-
1400	.6700	.3300	-	-	-
1500	.6700	.3300	-	-	-
2000	.6700	.3300	-	-	-
Experimental	.688	.259	.004	.018	.031
<u>Composition D</u>					
500	.0027	.0048	.2481	.7444	-
1000	.5151	.3030	-	.1818	.0001
1100	.6380	.2835	-	.0780	.0004
1200	.6916	.2746	-	.0315	.0022
1300	.7056	.2721	-	.0131	.0092
1400	.7008	.2641	-	.0057	.0294
1500	.6617	.2607	-	.0024	.0752
2000	.6262	.2525	-	-	.1212
Experimental	.704	.217	n.o.	.012	.068

TABLE IV (cont.)

Temperature °K	H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>
<u>Composition E</u>					
500	.0007	.0204	.3365	.6424	-
1000	.4490	.4081	-	.1428	.0001
1100	.5548	.3833	-	.0615	.0004
1200	.5983	.3752	-	.0243	.0022
1300	.6130	.3678	-	.0102	.0090
1400	.6046	.3628	-	.0044	.0282
1500	.5718	.3511	-	.0019	.0752
2000	.5000	.3300	-	-	.1700
Experimental	.648	.252	n.o.	.014	.087
<u>Composition F</u>					
500	.0008	.0176	.2583	.7233	-
1000	.5000	.3265	-	.1735	.0001
1100	.6157	.3079	-	.0759	.0004
1200	.6672	.2982	-	.0308	.0025
1300	.6896	.2882	-	.0124	.0099
1400	.6760	.2868	-	.0055	.0317
1500	.6394	.3552	-	.0023	.0842
2000	.5000	.2500	-	-	.2500
Experimental	.606	.303	n.o.	.013	.078

- &lt;0.0001

n.o. not observed